Orr. to FR 1.576.427

PATENT SPECIFICATION

1,172,967

DRAWINGS ATTACHED

1,172,967

Date of Application (No. 16808/68) and filing Complete Specification: 8 April, 1968.

Application made in Japan (No. 23321) on 12 April, 1967.

Complete Specification Published: 3 Dec., 1969.

Index at acceptance:—C3 P(4D3B1, 4K7, 4P1D, 4P3, 4P6G, 4T1C, 4T2G, 7D1A, 7K4, 7P1D, 7P3, 7P6G, 7T1C, 7T2G)

International Classification:—C 08 f 1/08, 3/56, 27/16

COMPLETE SPECIFICATION

Process for the preparation of Saponified Homopolymers of Vinyl Acetate and Copolymers of Ethylene and Vinyl Acetate

We, KURASHIKI RAYON KABUSHIKI KAISHA, a Japanese body corporate, of 1621, Sakazu, Kurashiki City, Japan, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of saponified homopolymers of vinyl acetate or copolymers of ethylene and vinyl acetate.

More particularly, the invention relates to a novel process for the preparation of saponified polyvinyl acetate or vinyl acetate-ethylene copolymer containing no more than 80 mol % of ethylene, which comprises polymerizing vinyl acetate or a vinyl acetate-ethylene mixture in an organic solvent by a solution polymerization method, separating the polymer formed from the organic solvent and unreacted vinyl acetate, and saponifying the polymer.

Polyvinyl alcohol and saponified vinyl acetate-ethylene copolymers are normally obtained by saponifying vinyl acetate homopolymer or copolymers of vinyl acetate with ethylene, respectively. In that case, if unreacted vinyl acetate remains in the polymerization reaction mixture, the saponified polymer is objectionably colored.

In order to prevent such phenomena, it is desirable to increase the conversion of vinyl acetate in the polymerization reaction closely to 100 %, and to use that polymerization product as the starting material in the saponification reaction. However, such complete polymerization requires an extremely long period and therefore inefficient, since the reaction rate decreases with the conversion of vinyl acetate and becomes very small when the conversion is near 100 %.

Therefore, substitution of the monomer in the reaction mixture with solvent before completion of the polymerization has been proposed, which is performed, for instance, as follows: a polyvinyl acetate solution containing unreacted monomer is continuously fed into the top portion of a rectifier-type column while an alcoholic vapor is introduced into the column from the bottom. Thus from the top an alcoholic solution of vinyl acetate is recovered, and from the bottom, an alcoholic solution of polyvinyl acetate is obtained, i.e. alcohol is substituted for vinyl acetate. However, in the above process, if methanol or ethanol is used as the alcohol, the vinyl acetate thereby replaced contains very minor amounts of aldehydes and acetic acid esters formed by the reaction with such alcohol. Repetitive recycling of such vinyl acetate, therefore, causes accumulation of the impurities therein, which in turn lowers the conversion of the material to polyvinyl acetate, and also causes coloration of the product polymers.

From the foregoing reasons, it can be understood that, in the preparation of polyvinyl acetate or vinyl acetate-ethylene copolymer, if the reaction is suspended, incomplete and unreacted vinyl acetate is recovered from the reaction mixture, the vinyl acetate monomer must be carefully isolated and purified before its recycling use.

As the means for separation and purification of vinyl acetate monomer, simple distillation is insufficient, since if a lower alcohol such as methanol or ethanol is used as the organic solvent in the preparation of polyvinyl acetate or vinyl acetate-ethylene copolymer, the alcohol forms an azeotropic mixture with vinyl acetate. In that case, the separation of vinyl acetate from the alcohol is achieved by extractive distillation using water as the separating agent. Furthermore, the thus recovered vinyl acetate

must be further distilled to remove the impurities therein, such as aldehydes, methyl or ethyl acetate, etc. Such extractive distillation and additional distillation procedures involve considerable expense, and are by no means acceptable to the industry.

The above objection is effectively eliminated by the present invention. The object of the invention, therefore, is to provide an economically advantageous process for the preparation of saponified homopolymers of vinyl acetate or copolymers of vinyl acetate and ethylene free from objectionable coloration, in which the loss of vinyl acetate is prevented and the above-mentioned refining procedures of the vinyl acetate are completely omitted.

The process of the invention comprises polymerizing vinyl acetate alone or together with ethylene in an organic solvent in the presence of a polymerization catalyst to form polyvinyl acetate or vinyl acetate-ethylene copolymers containing no more than 80 mol % of ethylene, evaporating the organic solvent by heating the reaction mixture, adding to the resultant polymer a lower aliphatic saturated alcohol (i.e. an aliphatic saturated alcohol having 1 to 4 carbon atoms), and saponifying the product in the presence of an alkali catalyst, thereby forming completely or partially saponified polyvinyl acetate or vinyl acetate-ethylene copolymer, characterized in that the polymerization is performed in tertiary butanol as the organic solvent, until the conversion of vinyl acetate to the polymer reaches 15—90 % by weight, and normal or basic cupric acetate is added to the reaction mixture, the system is subsequently heated to evaporate the tertiary butanol and vinyl acetate monomer and the tertiary butanol and vinyl acetate evaporated are recovered.

Hereinafter the subject process will be explained in further detail, taking the process steps in sequence and compared with conventional processes.

[1] Preparation of polyvinyl acetate or vinyl acetate-ethylene copolymer:

Solution polymerization of vinyl acetate alone, or together with ethylene, in an organic solvent such as methanol in the presence of a polymerization catalyst is known. As the catalyst, for example, the following are known to be useful: nitrogen compounds which form free radicals upon thermal decomposition, such as α,α' - azobisisobutyronitrile or α,α' - azobis(α,γ - dimethylvaleronitrile); and organic peroxides such as benzoyl peroxide and lauroyl peroxide.

In the process of the invention, in the preparation of polyvinyl acetate or vinyl acetate-ethylene copolymers containing no more than 80 mol % of ethylene (hereinafter they may be referred to briefly as vinyl acetate-ethylene copolymers) by polymerization of vinyl acetate alone or together with ethylene in an organic solvent in the presence of any of the above known catalysts, tertiary butanol is used as the organic solvent, and the polymerization reaction is suspended when the conversion of vinyl acetate to the polymer has reached 15—90 % by weight, preferably 20—80 %.

The polymerization step in accordance with the invention can be performed, for example, by charging a polymerization vessel with tertiary butanol and any of the foregoing catalysts, adding a predetermined amount of vinyl acetate, and heating the system to 40—60°C. normally at atmospheric pressure. The pressure may be elevated if desired. For copolymerization of vinyl acetate with ethylene, a predetermined amount of ethylene is supplied to the above polymerization system of vinyl acetate, according to the desired copolymerization ratio, with the ethylene pressure suitably adjusted. The copolymerization ratio is determined by such factors as polymerization temperature, ethylene pressure and the quantitative ratio between vinyl acetate and ethylene in the system. These specific conditions can be easily determined through experiments.

The lower limit of the ratio of tertiary butanol, which is the solvent, to vinyl acetate is determined by the minimum necessary amount of the solvent for smooth progress of the polymerization, while preventing or reducing formation of cross-linked polymers, viscosity rise in the reaction mixture and difficulties in removing the heat of polymerization caused by high viscosity. The upper limit of the ratio is determined by economics. The preferred ratio of tertiary butanol to vinyl acetate monomer is from 0.1 : 1 to 7 : 1 on a weight basis.

Conventionally, in the majority of the cases methanol is used as the organic solvent in the polymerization of vinyl acetate on an industrial scale, since it is the least expensive, and methanol solutions of polyvinyl acetate have low viscosities, making them convenient for transportation. However we discovered that use of methanol as solvent is subject to a number of objections, and that the use of tertiary butanol gives rise to various surprising advantages.

[2] Separation of vinyl acetate monomer and organic solvent from the product polymer:

In the process of the invention, the reaction mixture obtained from the above polymerization is heated, so that the tertiary butanol and unreacted vinyl acetate are evaporated, and recovered by condensation, thereby separating them from the polyvinyl acetate or vinyl acetate-ethylene copolymer formed in the polymerization.

The heating of the polymerization mixture may be carried out at a temperature higher than the boiling point of vinyl acetate under the operation pressure but lower than 150°C. Further, the heating may be carried out under atmospheric or reduced pressure. In short, the

heating may be carried out at any temperature at which tertiary butanol and vinyl acetate are efficiently evaporated and reaction between vinyl acetate and tertiary butanol does not occur to a substantial extent.

Any vessel to be usually used for treating highly viscous materials may be available as the container used in said heating. For instance, a thin film evaporator or an apparatus with a scraper for concentrating highly viscous materials can be used.

As previously described, the reaction mixture still contains a considerable amount of monomeric vinyl acetate. Therefore, in accordance with the invention, normal cupric acetate [$Cu(CH_3COO)_2$] or basic cupric acetate [$Cu(CH_3COO)_2CuO$] is added to the recation mixture in advance of the heating, in an amount of 1×10^{-5}—5×10^{-1}%, preferably 1×10^{-4}—5×10^{-2} %, by weight of the latter. Thus during the subsequent heating of the mixture for evaporation and recovery of monomeric vinyl acetate and tertiary butanol therefrom, polymerization of vinyl acetate is prevented effectively, and furthermore the reaction between vinyl acetate and tertiary butanol does not occur even in the presence of the above-mentioned copper salt. Therefore, objectionable side formation of aldehydes and acetic acid esters is substantially prevented. Consequently, the saponification of thus separated polyvinyl acetate or vinyl acetate-ethylene copolymer will yield products free from objectionable colors. Furthermore, the liquid mixture of the monomeric vinyl acetate and tertiary butanol recovered is substantially free from any by-product, and can be recycled to the polymerization system without intervening purification.

[3] Saponification of polyvinyl acetate or vinyl acetate-ethylene copolymer.

The polyvinyl acetate or vinylacetate-ethylene copolymer separated in the above step is formed into a homogeneous solution or a suspension in which the polymer is uniformly dispersed, by addition thereto of at least an equimolar amount, preferably at least 2 mols, per mol of the acetate radicals in the polymer, of an aliphatic saturated alcohol having 1—4 carbon atoms, and other organic solvent if necessary, in accordance with the conventional practice. To the solution then the required amount of alkali is added to entirely or partially saponify the polymer or copolymer, and the saponified product is duly recovered. The specific type of alcohol to be added to the reaction mixture is essentially not critical, as long as it is capable of inducing saponification of the polymer. Aliphatic saturated alcohols having 1—4 carbon atoms are used because of easy availability and handling, as well as low cost. The quantity of the alcohol is not critical, as long as it allows easy recovery of the saponified product.

As the optionally added organic solvent, an aromatic organic solvent such as benzene or toluene may be used, for example. Concurrent use of such organic solvent with the alcohol is useful for improving the solubility of the vinyl acetate - ethylene copolymer. For example, the copolymers containing no more than 61 mol % of copolymerized ethylene are soluble in methanol, but copolymers of higher ethylene contents are partially soluble or insoluble in methanol. In the latter case, it is preferred to add an aromatic organic solvent such as benzene or toluene to methanol, in order to improve the solubility of the copolymer. Preferably however, the copolymerization ratio will be adjusted so that the ethylene content of the copolymer is below 61 mol %.

As the alkali to be used in the saponification reaction, for example, alkali hydroxides such as sodium or potassium hydroxide, and lower alcoholates of alkali metals such as sodium methylate or ethylate, are suitable. The amount of the alkali is suitably determined, depending on the required degree of saponification, and copolymerization ratio of vinyl acetate to ethylene. Generally speaking, a greater amount of alkali is required for saponification of vinyl acetate-ethylene copolymer, than for saponification of polyvinyl acetate. The preferred temperature for the saponification is from room temperature to 140°C.

The entirely or partially saponified polyvinyl acetate or vinyl acetate-ethylene copolymer formed by the above saponification may precipitate in the reaction liquid, or remain dissolved, or partially precipitate and partially remain dissolved in the liquid, depending on such factors as the degree of saponification of the product and copolymerization ratio of vinyl acetate to ethylene.

If all of the saponified product precipitates, it can be separated by a known filtration method. If the whole or part of the product still remains in the reaction liquid as dissolved, a suitable non-solvent is added to the system to cause the precipitation of the saponified product. The precipitate can be recovered by filtration. Thus obtained product may be further removed of the liquid component if necessary, dried and used as the final product of the invention. The recovery of the saponified product can be performed by any known means.

As in the foregoing, the characteristics of the invention reside in the use of tertiary butanol as the organic solvent in the polymerization of vinyl acetate or copolymerization of vinyl acetate with ethylene; suspension of the polymerization reaction at a point when 15—90 % by weight of the vinyl acetate present in the system is converted to the polymer or copolymer; and in the process of recovering tertiary butanol and unreacted vinyl acetate from the resultant reaction mixture, comprising adding normal or basic cupric acetate to the reaction

mixture and heating the system, so as to evaporate and recover tertiary butanol and unreacted vinyl acetate.

In previous attempts to recover unreacted vinyl acetate and organic solvent by heating the reaction mixture resulting from polymerization of vinyl acetate or copolymerization of vinyl acetate with ethylene in an organic solvent in the presence of a catalyst, a polymerization-retarder or -inhibitor has been added to the reaction mixture before the heating, in order to prevent polymerization of vinyl acetate during the heating. However, most conventional polymerization-inhibitors tend to bring about coloration in the saponified products.

We have found however that cupric acetate, normal or basic, is much less liable to bring about the coloration and exhibits a better polymerization-inhibiting effect than the conventional polymerization-inhibitors referred to above.

Neither normal cupric acetate nor basic cupric acetate can escape from the defect that they promote to a substantual extent the reaction of vinyl acetate with a lower alcohol such as methanol, ethanol, n-propanol, iso-propanol, n-butanol and sec.-butanol and as a result formation of acetic acid esters or aldehydes is increased.

However, we have also found that tertiary butanol does not react with vinyl acetate at all at a temperature below 150°C. even if the cupric acetate is present. Thus, the following advantages have been brought about by the present invention:

1. the polymerization of vinyl acetate is substantially inhibited during the heating step;

2. the reaction between tertiary butanol and vinyl acetate can be very effectively prevented;

3. accordingly, the recovered liquid mixture of tertiary butanol and vinyl acetate can be repeatedly recycled to the initial polymerization step without an intervening purification step;

4. the omission of the intervening purification step gives the advantage in reduction of the required heat; and

5. colorless or substantially colorless saponified products can be obtained by the saponification described above.

Fig. 1 of the accompanying drawings illustrates that reaction of vinyl acetate with methanol, is substantial in the presence of cupric acetate, while the reaction does take place only slightly in the absence of catalyst. Referring to Fig. 1, the axis of abscissa denotes reaction time and that of ordinate, methyl acetate concentration formed in the reaction liquid. The curves A and B show the relation between the quantities of methyl acetate formed and reaction time, when 0.1 % and 0.001 % by weight, respectively, of $Cu(CH_3COO)_2 . H_2O$ are added to the system. In both cases (A and B), the mol ratio of methanol to vinyl acetate is 1:1, and the reaction temperature is 55°C.

In contrast to the results indicated in Fig. 1, no reaction between tertiary butanol and vinyl acetate takes place below 150°C., even in the presence of normal or basic cupric acetate.

Fig. 2 of the accompanying drawings illustrates schematically one method of carrying out the process of the invention. Vinyl acetate and tertiary butanol are fed to polymerization vessel 1 through pipe 12. Pipe 5 is for ethylene supply, which is used in the case of copolymerization of vinyl acetate with ethylene. The polymerization is performed under the previously described conditions, and the reaction liquid is transferred to ethylene desorber 2 through pipe 7; at the pipe 13 cupric acetate is added to the reaction liquid in the form of, for example, a tertiary butanol solution of cupric acetate. In case of vinyl acetate-ethylene copolymerization, substantially all the ethylene is desorbed in the vessel 2 by such means as reducing the pressure and returned to the reactor 1 via pipe 6 while the remaining system is sent to separator 3 through pipe 8. The separator consists of, for example a thin film evaporator or an apparatus suited for concentration of a higly viscous substance, for example, a scraped wall reactor. The polymer or copolymer separated at the apparatus 3 is withdrawn through pipe 10. The unreacted vinyl acetate and tertiary butanol also separated at the apparatus 3 is sent to a condenser 4 through pipe 9, and the condensed solution is recycled through pipe 11, without an intervening purification step. The withdrawn polymer or copolymer is transferred to the saponification vessel 14 and dissolved in methanol supplied from pipe 15. The saponified polymer or copolymer formed in the presence of an alkali catalyst is withdrawn through pipe 16.

Thus in accordance with the invention, polyvinyl acetate or vinyl acetate-ethylene copolymer containing no more than 80 mol % of ethylene, which is saponified to any desired degree and is free of objectionable coloration, is obtained with economic advantages. The entirely or partially saponified products possess a wide range of utilities, as starting materials for fibres, films and other shaped products, or as a paint base, etc.

Particularly because the saponified products of the copolymer containing no more than 80 mol % of ethylene exhibit little oxygen-permeability, they are useful as in making oxygen-shielding shaped products, such as food-packaging film.

EXAMPLES 1 and 2 and CONTROLS 1—9

In these Examples, the excellent polymerization-inhibiting action of normal or basic cupric acetate is illustrated in comparison with other known inhibitors, and they also show that the inhibitor of this invention is useful to drastic-

ally reduce the degree of coloration in the saponified polyvinyl acetate or ethylene-vinyl acetate copolymer, even after thermal treatments.

A vinyl acetate-tertiary butanol mixture, in which the weight ratio of tertiary butanol to vinyl acetate was 0.65, was supplied to a polymerization vessel, and continuously copolymerized with ethylene at an ethylene pressure of 36 kg/cm²G, at 60°C., in the presence of azobis-isobutyronitrile as the catalyst. From the reaction mixture continuously withdrawn from the polymerization vessel, the ethylene absorbed was desorbed. The remaining solution consisted of 47 wt. parts of ethylene-vinyl acetate copolymer, 54 wt. parts of tertiary butanol, and 40 wt. parts of unreacted vinyl acetate. To that reaction mixture, each of the polymerization-inhibitors listed in Table 1 was added in an amount of 5×10^{-4} wt. % of the vinyl acetate, and each resultant mixture was sent to the polymer-separator. At 110°C. and 600 mm Hg, the unreacted vinyl acetate and tertiary butanol were removed, and the copolymer was continuously withdrawn. The ethylene content of the copolymer was, in all cases 35 mol %. The copolymer was dissolved in methanol to form a solution containing 22% by weight of copolymer. After caustic soda was added to the polymer solution in such an amount that the mol ratio of the caustic soda to the acetate groups contained in the copolymer was 0.3:1, the saponification was carried out at a temperature of 60°C. over a period of 2.5 hours. The resulting saponified product exhibited a saponification degree of 98.5 mol %.

The saponified polymer thus obtained was shaped into pellets by conventional melt-extrusion, and the coloration thereof was judged by the stimulus value Z obtained by measuring the surface color by a reflection method in accordance with JIS Z8701. The rating of the degree of coloration is given in Table 1 read in conjunction with Table 2.

The polymeric pellets were shaped into 60 cm-wide films through a melt-extruder equipped with a T-shaped die, and the number of fish eyes in each film was counted. The results are given in Table 1 read in conjunction with Table 3. The significance of the number of fish eyes is now explained. Since in the step of separating unreacted monomeric vinyl acetate and tertiary butanol, ethylene has been already desorbed and eliminated, if the polymerization-inhibiting effect of the inhibitor added is small, homopolymer and homo-oligomer of vinyl acetate is formed and mixed with the ethylene-vinyl acetate copolymer. Therefore, when the saponified polymeric mixture is formed into a film, both saponified ethylene-vinyl acetate copolymer and saponified vinyl acetate homopolymer would be present in the film. Since the two polymers have little compatibility, the film would develop fish eyes. Accordingly, the smaller the number of fish eyes in the film, the greater the effectiveness of the polymerization-inhibitor employed.

TABLE 1
Degree of Coloration- and Polymerization-inhibiting Effects of Polymerization-inhibitors

Run	Polymerization-inhibitor	Degree of coloration of pellet	Rating of fish eyes in film
Example 1	Cupric acetate (normal)	I	I
„ 2	Cupric acetate (basic)	I	I
Control 1	Copper naphthenate	IV	III
„ 2	Cupric chloride	IV	I
„ 3	Copper resinate	IV	III
„ 4	Cupric sulfate (anhydrous)	IV	III
„ 5	Cupric nitrate	IV	I
„ 6	Cuprous acetate	I	V
„ 7	Hydroquinone	V	IV
„ 8	Thiodiphenylamine	V	IV
„ 9	Thiourea	III	IV

TABLE 2

Index number of degree of coloration	Stimulus value Z*
I	45≦Z <100
II	35≦Z < 45
III	25≦Z < 35
IV	15≦Z < 25
V	0≦Z < 15

*Stimulus values Z were obtained by measuring the surface color of the sample pellets having a thickness of 8—10 mm by a reflection method in accordance with JIS Z8701.

TABLE 3

Rating of fish eyes in film	Number of fish eyes present in 100 cm² of film
I	less than 15
II	15—80
III	80—160
IV	150—300
V	more than 300

From the results given in Table 1, it can be understood that normal and basic cupric acetate used as the polymerization-inhibitors in accordance with this invention exhibit much higher inhibiting action than those of other inhibitors, and at the same time the saponified copolymers produced by the process of the invention are substantially free from coloration. Whereas, monovalent cuprous acetate (not a polymerization-inhibitor used in the process of this invention) produced a good reduction is coloration, it had an extremely inferior effect in inhibiting polymerization, and is thus unsatisfactory for practical use.

EXAMPLE 3 and CONTROLS 10—13

To equimolar mixtures of various lower aliphatic alcohols with vinyl acetate, 0.1 wt. % based on each mixture of normal or basic cupric acetate was added, and each system was reacted at 55°C. for 60 minutes and 120 minutes. The quantity of acetic acid ester thus formed by the ester-interchange reaction between vinyl acetate and each specified alcohol was determined. The results are shown in Table 4 below.

TABLE 4

Acetic Acid Ester in Reaction Liquid

(percent by weight)

Run	Solvent \ Reaction time \ Cupric salt	Normal cupric acetate		Basic cupric acetate	
		60 min.	120 min.	60 min.	120 min.
Example 3	t-butanol	trace	trace	trace	trace
Control 10	methanol	11.2	13.0	10.6	12.4
„ 11	ethanol	8.7	10.2	8.1	9.5
„ 12	n-propanol	7.5	9.2	7.2	8.5
„ 13	sec.-butanol	6.1	8.3	5.8	7.6

The results of the table above clearly indicate that in the presence of normal or basic cupric acetate, ester-interchange reaction between lower aliphatic alcohols, except between tertiary butanol and vinyl acetate, does take place to a considerable degree, but tertiary butanol is outstanding in that it does not undergo the reaction. For this reason it is possible to achieve the very favourable results of this invention, by the concurrent use of tertiary butanol as the polymerization solvent, with normal or basic cupric acetate or a mixture thereof as the polymerization-inhibitor.

EXAMPLE 4

Vinyl acetate was supplied to a polymerization vessel while the mixture of vinyl acetate and tertiary butanol which was separated from the reaction mixture and withdrawn from the vessel was recycled to the same vessel, and the weight ratio of tertiary butanol to vinyl acetate was adjusted to 0.45. The polymerization was performed continuously at 40°C. and atmospheric pressure, in the presence of azo-bis-isobutyronitrile as the catalyst. The resultant reaction liquid consisted of 46 wt. parts of vinyl acetate, 45 wt. parts of tertiary butanol and 54 wt. parts of polyvinyl acetate. To the reaction liquid, 0.001 wt. % thereof of normal cupric acetate was added, and the system was transferred to a polymer separator. Under the conditions of 110°C. and 600 mm Hg pressure, unreacted vinyl acetate and tertiary butanol were removed, and polyvinyl acetate was continuously withdrawn. The mixture of vinyl acetate and tertiary butanol recovered in that stage was recycled to the polymerization vessel without purification. The polyvinyl acetate was dissolved in methanol to form a solution having a polymer concentration of 10% by weight. After caustic soda was added to the polymer solution in such an amount that the mol ratio of the caustic soda to the acetate groups in the polymer was 0.01, the saponification of the polymer was carried out at a reaction temperature of 50°C. for 30 minutes. The degree of saponification of the product was 99%. The average degree of polymerization of the product was 5,200. Even when the weight ratio of the polymer formed to the tertiary butanol employed reached 1000: 1, no formation or accumulation of the reaction product of vinyl acetate and tertiary butanol was observed in the recycled mixtures of vinyl acetate and tertiary butanol. The saponified product was pelletized using water as an assistant, and the stimulus value Z (see Examples 1 and 2) was measured. The pellets were observed to have a stimulus value Z of 49. No coloration of the saponified product was observed.

EXAMPLE 5

Example 4 was repeated except that basic cupric acetate was added as the polymerization-inhibitor, in an amount of 0.01%, and the mixture of unreacted vinyl acetate and tertiary butanol was separated from polyvinyl acetate at 120°C., and 750 mm Hg. pressure. Even when the weight ratio of the polymeric product to the tertiary butanol employed reached 5000: 1, still no accumulation of reaction product of vinyl acetate and tertiary butanol was recognized. The stimulus value Z of the pellet of the saponified product measured in accordance with JIS Z8701 was 46, and hardly any coloration was observed.

EXAMPLE 6

Vinyl acetate was supplied to a polymerization vessel and a recovered liquid mixture of vinyl acetate and tertiary butanol was added, the weight ratio of tertiary butanol to vinyl acetate being 0.4:1. The polymerization was performed continuously at an ethylene pressure of 30 kg/cm^{2}G and at 57°C., in the presence of azobis-isobutyronitrile as the catalyst. The reaction liquid continuously withdrawn from the polymerization vessel was first stripped of the ethylene absorbed, and then transferred into a polymer separator. The ethylene from the stripper was recycled to the polymerization vessel. The reaction liquid consisted of 52 wt. parts of ethylene-vinyl acetate copolymer, 40 wt. parts of tertiary butanol and 55 wt. parts of unreacted vinyl acetate. To the liquid, 0.005 wt. % of normal cupric acetate was added, and the system was transferred to a polymer separator. At 115°C. and 650 mm Hg, unreacted vinyl acetate and tertiary butanol were removed from the system, and remaining copolymer was continuously withdrawn. The ethylene content of the copolymer was 31.5 mol %. The liquid mixture of the unreacted vinyl acetate and tertiary butanol was recycled to the polymerization vessel without any refining. The copolymer was dissolved in methanol to form a solution having the copolymer concentration of 25% by weight and to the solution caustic soda was added in such an amount that the molar ratio of the caustic soda to the acetate groups in the copolymer was 0.3:1. Thereafter, the saponification was carried out at 60°C. for 3 hours. The degree of saponification of the product was 98%. The intrinsic viscosity of the saponified copolymer measured in aqueous phenol containing 15 wt. % of water at 30°C., [η], (hereinafter the conditions under which the intrinsic viscosity was measured are identical) was 0.125 l/g.

Even when the weight ratio of the copolymer formed to the tertiary butanol used reached 4000:1, no accumulation of reaction products of vinyl acetate with tertiary butanol was recognized in the liquid mixture recovered from the polymer separator. A film of 25μ thickness prepared from the saponified product demonstrated a fish eye number of 3 in 100 cm^2. Further, the saponified product contained no polyvinyl alcohol incorporated therein. The stimulus value Z of the pellet prepared from the saponified product measured in accordance with JIS Z8701 was 47, and no coloration was observed on the pellet.

EXAMPLE 7

Example 6 was repeated except for the following changes: the ethylene pressure was increased to 59 kg/cm^{2}G; the initial weight ratio of tertiary butanol to vinyl acetate was 0.55, and the amount of normal cupric acetate was 0.01% to the reaction liquid. The reaction liquid stripped of ethylene consisted of 79 wt. parts of ethylene-vinyl acetate copolymer, 55 wt. parts of tertiary butanol and 45 wt. parts of unreacted vinyl acetate. The ethylene content of the copolymer was 57.2 mol %, and the degree of saponification of the product was 97%. The saponified product had an [η] of 0.083 l/g. The stimulus value Z of the pellet prepared from the saponified product measured in the same manner as in Example 6 was 48.

Even when the weight ratio of the copolymer to the tertiary butanol employed reached 2000:1, no accumulation of reaction product of vinyl acetate with tertiary butanol in the liquid mixture recovered from the polymer separator was recognized. The saponified product contained no polyvinyl alcohol, and was free from coloration.

EXAMPLE 8

Together with a recovered liquid mixture of vinyl acetate and tertiary butanol, vinyl acetate was fed to a polymerization vessel in such an amount that the weight ratio of the tertiary butanol to the vinyl acetate was 0.85. The continuous polymerization was carried out under an ethylene pressure of 85 kg/cm^2 at a polymerization temperature of 60°C. in the presence as the catalyst of α,α'-azobisbutyronitrile. The amount used of the catalyst was 0.3% by weight based on the vinyl acetate fed. The reaction liquid continuously withdrawn from the polymerization vessel was stripped of the ethylene absorbed and then transferred into a polymer separator. The stripped ethylene was recycled to the polymerization vessel. The reaction liquid consisted of 83.5 parts by weight of ethylene-vinyl acetate copolymer, 80 parts by weight of tertiary butanol and 51.6 parts by weight of unreacted vinyl acetate. The ethylene content of the copolymer was 74.2 mol %. To the liquid 0.03% by weight of normal cupric acetate was added, and the system was transferred to a polymer separator. At 1770°C. and 610 mm Hg pressure unreacted vinyl acetate and tertiary butanol were recovered from the system and the remaining copolymer was continuously withdrawn. The so recovered liquid mixture of unreacted vinyl acetate and tertiary butanol was recycled to the polymerization vessel without refining thereof as the stripped ethylene was recycled.

Even when the weight ratio of the copolymer formed to the tertiary butanol used reached 1000:1, no accumulation of reaction products of vinyl acetate with butanol was recognized.

The so prepared copolymer was saponified under varying saponification conditions as specified in Table A and saponified products having saponification degrees shown in Table A were obtained from said copolymer. The saponified products having saponification degrees higher than 90 mol % were respectively shaped into film of 25μ thickness. The

number of fish eyes appearing in each of the films was less than 10 in 100 cm^2.

TABLE A

Ethylene content in copolymer (mol %)	74.2	74.2	74.2	74.2	74.2	74.2	74.2
Solvent in saponification system	methanol 30 wt. % t-butanol 70 wt. %	methanol 40 wt. % toluene 60 wt. %	ethanol 32 wt. % t-butanol 68 wt. %	methanol 50 wt. % toluene 50 wt. %	ethanol 40 wt. % benzene 60 wt. %	t-butanol 100 wt. %	n-propanol 50 wt. % toluene 50 wt. %
Concentration of copolymer at the beginning of the reaction (wt. %)	20.5	21.0	20.7	22.0	22.0	21.5	21.5
Time for saponification (hr.)	3.1	3.0	5.0	3.0	5.0	2.0	6.5
NaOH mol ratio*	0.7:1	0.6:1	1.0:1	0.8:1	0.8:1	0.4:1	0.8:1
Saponification temperature (°C.)	65	60	65	63	65	70	70
Saponification degree of saponification product (mol %)	85.8	90.8	96.3	97.4	88.2	42.2	95.1
Coloration of saponified product** (pellet)	47	46	49	49	48	—	47
Number of fish eyes in film (25μ) prepared by melt shaping saponified product (per 100 cm^2)	—	<10	<10	<10	—	—	<10

* the mol ratio of the caustic soda used to the acetate groups contained in the copolymer.

** based on the stimulus value Z: obtained by measuring the surface color by a reflection method and was indicated in accordance with JIS Z8701.

As is clear from stimulus values Z shown in Table A above, hardly any coloration was observed in pellets prepared from saponified products of the copolymer obtained in this Example.

EXAMPLE 9

The copolymer prepared by repeating the procedures of Example 7 was dissolved into a mixed solvent consisting of 75 parts by weight of methanol and 25 parts by weight of secondary butanol in such an amount that the concentration of the polymer was 23% by weight. To the so prepared copolymer solution was added sodium methylate in such an amount that the mol ratio of the sodium methylate to the acetate groups contained in the copolymer was 0.03. The saponification was carried out at 60°C. over a period of 2 hours. The resulting saponified product had a saponification degree of 95.6 mol % and an intrinsic viscosity [η] of 0.120 liter/g. The stimulus value Z of the pellet prepared from said saponified product was 46 and no coloration thereof was observed.

Even when the weight ratio of the copolymer formed to the tertiary butanol used reached 2000: 1, no accumulation of reaction producrs of vinyl acetate to tertiary butanol was recognized in the recovered mixture liquid of vinyl acetate and tertiary butanol. The number of fish eyes appearing on the film of 25 μ thickness prepared from the saponified product was only 5 per 100 cm², and the saponified product contained no polyvinyl alcohol.

EXAMPLE 10

Example 4 was repeated except the solvent in the saponification of polyvinyl acetate was varied each time to ethanol, n-propanol, n-butanol, iso-butanol and sec.-butanol. In each case saponified polyvinyl acetate having a saponification degree of 97.99% was obtained similarly to Example 4. All the products were completely free from coloration.

WHAT WE CLAIM IS:—

1. Process for the preparation of entirely or partially saponified polyvinyl acetate or vinyl acetate-ethylene copolymer by the steps of polymerising vinyl acetate alone or together with ethylene in an organic solvent in the presence of a known polymerisation catalyst, to form polyvinyl acetate or vinyl acetate-ethylene copolymer containing no more than 80 mol % of ethylene, heating the resultant reaction mixture to evaporate the organic solvent, adding to the polymeric product a lower aliphatic saturated alcohol in an amount at least equimolar to the acetate radical in the polymer, and saponifying the product in the presence of an alkali catalyst, characterised in that the polymerization is performed in tertiary butanol as the organic solvent, until the conversion of vinyl acetate to the polymer reaches 15—90% by weight, normal or basic cupric acetate is added to the polymeric mixture obtained, the system is subsequently heated to evaporate the tertiary butanol and vinyl acetate monomer therein and the tertiary butanol and vinyl acetate evaporated are recovered.

2. A process according to claim 1, wherein the vinyl acetate monomer and the tertiary butanol recovered are recycled to the polymerisation process without any intervening purification.

3. A process according to claim 1 or 2, wherein the polymerisation reaction is suspended when the conversion of the vinyl acetate into the polymer reaches 20—80% by weight.

4. A process according to any preceding claim, wherein vinyl acetate is copolymerised with ethylene and the ratio of vinyl acetate to ethylene is such that the ethylene content of the resulting vinyl acetate-ethylene copolymer is below 51 mol %.

5. A process according to any preceding claim, wherein the lower aliphatic saturated alcohol is methanol.

6. A process according to any preceding claim, wherein the heating for evaporating the vinyl acetate and the tertiary butanol is carried out at a temperature higher than the boiling point of vinyl acetate under the pressure adopted in the heating procedure but lower than 150°C.

7. A process according to claim 1, wherein the weight ratio of the tertiary butanol to vinyl acetate during the polymerisation is from 0.1: 1 to 7: 1.

8. A process according to claim 1, substantially as hereinbefore described with reference to the Examples.

9. Saponified vinyl acetate polymers obtained by a process claimed in any preceding claim.

J. A. KEMP & CO.,
Chartered Patent Agents,
14 South Square.
Gray's Inn, London, W.C.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

Fig. 1

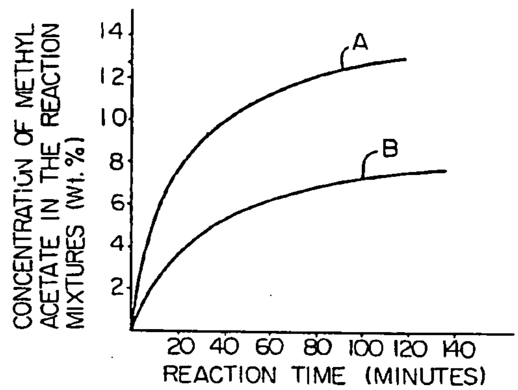
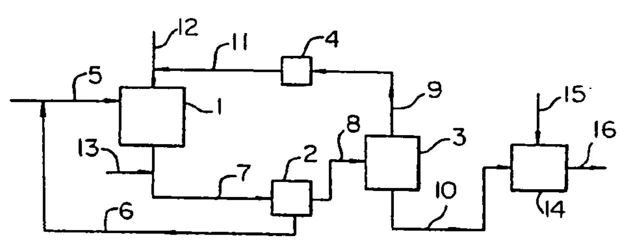

CONCENTRATION OF METHYL ACETATE IN THE REACTION MIXTURES (Wt. %)
14
12
10
8
6
4
2
A
B
20 40 60 80 100 120 140
REACTION TIME (MINUTES)

Fig. 2


12
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14
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